Construction of a Liquid Membrane Type Benzethonium Ion Sensitive Electrode and its Application to the Potentiometric Titration of Some Anionic Detergents

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Construction of a liquid membrane type benzethonium (benzyltrimethyl [2-[2(*p*-1,1,3,3-tetramethylbutylphenoxy)-ethoxy]ethyl] ammonium chloride, $C_{27}H_{42}ClNO_2$) ion sensitive electrode and its application to potentiometric titration of anionic detergents are described. The electrode was prepared by using nitrobenzene extract of benzethonium-tetraphenylborate ion-pair as an ion-exchange membrane. The electrode shows the Nernstian response to benzethonium cation in the concentration range from 10^{-3} to 10^{-7} M. Electrode potential showed almost constant value in the pH range from 2 to 12 at the 5×10^{-4} M benzethonium cation concentration. Effects of diverse ions were evaluated and [metal ions did not interfere, but some quaternary onium cations showed strong interference. The present electrode was successfully applied to the potentiometric titrations of some anionic detergents and the results showed good agreement with the familiar Epton method.

1 Introduction

Nowadays, many liquid membrane type ion-selective electrodes sensitive to organic ions were reported. Anionic surfactant ion-selective electrode, *i.e.*, octyl sulfate¹⁾, dodecyl sulfate¹⁻⁴⁾, benzenesulfonate^{4,5)}, toluenesulfonate^{6,7)}, dodecylbenzenesulfonate⁶⁻¹¹⁾, naphthalenesulfonate^{5,12)}, tetraphenylborate¹³⁾, bis-(2-ethylhexyl) sulfosuccinate¹⁴⁾ ion-selective electrodes were constructed and some of them were applied to the determination of ionic surfactants.

Benzethonium chloride ($C_{27}H_{42}ClNO_2$, abbreviated as Benz⁺Cl⁻) (Hyamine 1622) is adopted to Japan Industrial Standard¹⁵⁾ as the standard reagent for cationic surface-active substance. In this paper, a liquid membrane type benzethonium ion sensitive electrode constructed by using nitrobenzene extract of benzethonium-tetraphenylborate (abbreviated as TPB) ion-pair as an ion-exchange membrane is described. The present electrode was successfully applied to the potentiometric titration of anionic surfactants.

2 Results and Discussion

2.1 Reagent

Ag/AgCl Electrode	Internal	Liquid Ion-exchanger	Sample	SCE
	Ref. Soln.	1 mM Benz ⁺ -TPB ⁻	Soln. of	
	1 mM Benz ⁺	in Nitrobenzene	Benz ⁺	
Ion Sensitive Electrode				

Benzethonium chloride monohydrate was obtained from wako Pure Chemicals Co. and a 0.01 M standard solution was prepared by dissolving 4.6611 g of reagent in 1 dm³ of deionized water. The solution was potentiometrically standardized against 0.01 M silver nitrate solution by the aid of silver electrode and stored in refrigerator. Sodium tetraphenylborate was obtained from Dojindo Laboratories and the certified purity of reagent was higher than 99.7%. Stock solution of 0.01 M sodium tetraphenylborate was prepared by dissolving 3.4223 g of the reagent into 1 dm³ of water and the solution was stored in refrigerator. The pH of tetraphenylborate solution was kept to 8.5 by adding Britton-Robinson buffer, because it decomposes gradually in acidic milieu.

2.2 Potential measurement

All the potential measurements were carried out by using a Corning Digital 110 pH Meter equipped with a Hitachi Recorder, 056. A Corning saturated calomel electrode, 476109, was used throughout the study. The composition of the present cell system including the present ion sensitive electrode is as follows.

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Key Words: Benzethonium Chloride, Ion Sensitive Electrode, Potentiometric Titration, Anionic Detergent

The cell assembly was the same as that described elsewhere^{16,17)}. The potential of ion sensitive electrode in the presence of foreign ions is given by the Nikolskii-Eisenman equation¹⁸⁾.

$$E = E^{\circ} + \frac{2.303 RT}{F} \times \log (a_{\text{Benz}^+} + \sum_j K_j \cdot a_j^{1/z_j}) \quad (1)$$

where E° is a constant, a_{Benz^+} and a_j are the activities of the object and j -th ion, K_j is the selectivity coefficient and z_j is the absolute value of charge on the ion j .

2.3 Preparation of liquid ion-exchange membrane

The liquid ion-exchange membrane was prepared by the solvent extraction of ion-pair of benzethonium cation and tetraphenylborate anion. To a 10 cm³ of 1.0 mM Benz⁺Cl⁻ solution in a 100-cm³ separatory funnel were added 10 cm³ of 1.0 mM Na⁺TPB⁻ solution and 10 cm³ of nitrobenzene. The mixture was shaken for 10 min and then let stand for 30 min. The organic phase was separated and then anhydrous sodium sulfate was added for the purpose of removing the water. Concentration of the ion-pair in the nitrobenzene extract was 1 mM.

2.4 Selection of counter anion

Anions of five kinds, *i.e.*, tetraphenylborate, bis-(2-ethylhexyl) sulfosuccinate (EHSS), dodecylbenzenesulfonate (DBS), chromazurol S (Ch. S), and pyrocatechol violet (PV), were used as the counter anion of ion-pair. All the concentration of ion-pair in the ion-exchange membrane is prepared to 1 mM. The slope of the calibration curve and their range of straight line are tabulated in Table 1.

Table 1 Selection of the ion-exchange site

Ion-exchange site	Slope (mV/decade)	Linear range (-log [Benz ⁺])
EHSS	58	4—6
DBS	51	4—7
Ch.S	53	3—5
PV	25	3—6
TPB	59	3—7

EHSS : Bis-(2-ethylhexyl) sulfosuccinate, DBS : Dodecylbenzenesulfonate, Ch.S : Chromazurol S, PV : Pyrocatechol violet, TPB : Tetraphenylborate

Tetraphenylborate anion was adopted as the counter anion, because of its wide linear range

and suitable slope (59 mV/activity decade) of calibration curve.

2.5 Selection of Benz⁺-TPB⁻ ion-pair concentration in the ion-exchange membrane

Calibration curves of various ion-pair concentrations are shown in Fig. 1. The electrode constructed with an extract of 0.01 mM ion-pair concentration was not suitable, because of

Fig. 1 Selection of Benz⁺Cl⁻ ion-pair concentration

Ion-pair concentration in nitrobenzene : —●— 10, —○— 1.0, —▲— 0.1 mM. Internal reference electrode : Ag/AgCl electrode, Internal reference solution : 1.0 mM Benz⁺Cl⁻, Temp. 18.5°C

the very poor potential stability. The membrane consisting of 1.0 mM ion-pair was found to be the most suitable.

2.6 Selection of internal reference electrode

Four kinds of internal reference electrode, *i.e.*, platinum, platinized platinum, silver, and silver-silver chloride electrode, are tested and the results are shown in Fig. 2. Platinum and platinized platinum electrodes showed relatively poor potential stability and their calibration curves are not straight. Silver-silver chloride electrode was adopted because it gave a good calibration curve. As the internal reference solution, a 1.0 mM Benz⁺Cl⁻ solution was found to be most suitable.

2.7 Effect of pH

Effect of pH on the EMF of the ion sensitive electrode was evaluated. Concentration of Benz⁺Cl⁻ in sample solution was 5 μM and 0.5 mM. The total ionic strength was kept at 0.1 M by adding sodium chloride and pH was adjusted

Fig. 2 Selection of internal reference electrode

Internal reference electrode: —●— Ag/AgCl, —○— Ag, —▲— Pt, —△— Pt-Pt electrode, Ion-pair concentration: 1.0mM, Temp. 18.5°C

by adding 0.1 M hydrochloric acid or sodium hydroxide containing the same concentration of object ion. As shown in Fig. 3, the EMF of the present cell was independent of pH from 2 to 11 for the both levels of benzenethonium ion concentration. As to the potential stability of the present electrode, the potential at 10^{-7} M Benz⁺Cl⁻ sample solution was shifted about +10 mV during 40 min. The reason for this fact seems to be an increase in

Fig. 3 Electrode response as a function of pH

Sample solution: —●— 0.5 mM, —○— 5 μM of Benz⁺Cl⁻ containing sodium chloride, hydrochloric acid or sodium hydroxide, Ionic strength: 0.1 M

benzethonium ion concentration in the sample solution and/or decrease in Benz⁺-TPB⁻ ion-pair concentration at the surface of ion-exchange membrane. With benzethonium sample solution higher than 10^{-6} M, the EMF was stable during 40 min.

2.8 Selectivity

Selectivity coefficients of the benzethonium ion sensitive electrode was evaluated by the familiar mixed solution method¹⁹⁾ and the results are tabulated in Table 2. Monovalent and divalent

Table 2 Selectivity coefficient for Benz⁺ ion sensitive electrode

Cation	$-\log K_j$	Cation	$-\log K_j$
Zeph ⁺	-0.27	Na ⁺	3.64
CP ⁺	-0.13	Fe ²⁺	3.88
TMA ⁺	2.33	Fe ³⁺	4.05
L-Phenylalanine ⁺	2.88	Ca ²⁺	4.32
L-Cystine ⁺	3.47	Cu ²⁺	4.55
NH ₄ ⁺	3.47	L-Histidine	4.65
K ⁺	3.61		

Zeph⁺: Benzyltrimethyltetradecylammonium cation, CP⁺: Cetylpyridinium cation, TMA⁺: Tetramethylammonium cation

metal ions do not interfere. The electrode shows, however, only a poor selectivity to some quaternary onium cations.

2.9 Potentiometric titration

The present electrode has been successfully applied to potentiometric titration of some anionic surfactants. The titration curves of Benz⁺Cl⁻ solution with Na⁺TPB⁻ solution are shown in Fig. 4. Potential jump of the titration curve at the end-point of 1 mM Benz⁺Cl⁻ solution with the same concentration of Na⁺TPB⁻ solution is almost 400 mV. The reason of such a great magnitude of potential jump is that the present electrode is sensitive to Benz⁺ cation as well as TPB⁻ anion. Titration of 10^{-6} M Benz⁺ solution with TPB⁻ solution of the same concentration is feasible. Some anionic detergents are titrated and the results are compared with Epton method^{20,21)}. Anionic detergents containing kitchen cleaning materials of "Family" and "Cherina" were also potentiometrically titrated. As shown in Table 3, the method based on the use of present electrode gives results within 2.6% in relative difference of those obtained

Fig. 4 Potentiometric titration curves of 10 cm³ portions of Benz⁺Cl⁻ solution with standard Na⁺TPB⁻ solution

—●—: Ca. 1 mM Benz⁺Cl⁻ titrated with 1.00 mM Na⁺TPB⁻, --○--: Ca. 0.1 mM Benz⁺Cl⁻ titrated with 0.100 mM Na⁺TPB⁻, —△—: Ca. 0.01 mM Benz⁺Cl⁻ titrated with 0.0100 mM Na⁺TPB⁻

Table 3 Comparison of the determinations of anionic detergents

Sample	10.0 mM Benz ⁺ Cl ⁻ required/cm ³		Relative difference (%)
	Present method	Epton method	
EHSS ⁻	9.06±0.01	9.25±0.02	2.1
DBS ⁻	9.15±0.03	9.22±0.03	0.8
DS ⁻	9.94±0.01	9.95±0.02	0.1
Family ^a	9.45±0.01	9.45±0.02	0
Cherina ^b	12.07±0.03	12.39±0.02	2.6

EHSS: Bis-(2-ethylhexyl) sulfosuccinate, DBS: Dodecylbenzenesulfonate, DS: Dodecyl sulfate, a: Kao Soap Co., diluted 40 fold, b: Kao Soap Co., diluted 50 fold. Number of titrations was five

by Epton method.

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(Received Mar. 15, 1982; Accepted Jul. 31, 1982)